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(54) PLASMA CORROSION RESISTANT MEMBER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a member more excellent in corrosion resistance to plasma and having a long service life by forming a member from an aluminum nitride sintered compact having a specified average grain diameter and specifying the average surface roughness of the surface of the member brought into contact with plasma.

SOLUTION: A member is formed from an aluminum nitride sintered compact having 1-20 μm average grain diameter and the average surface roughness of the surface of the member brought into contact with plasma is reduced to ≤0.5 μm. The aluminum nitride sintered compact is obtd. as usual. In order to very smoothly finish the surface brought into contact with plasma, grinding and/or polishing is adopted. Since aluminum nitride has much higher heat conductivity and a lower coefft. of thermal expansion than alumina, large thermal stress is less liable to occur in aluminum nitride and excellent corrosion resistance to plasma and a long service life are ensured.

LEGAL STATUS

[Date of request for examination]

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CLAIMS

[Claim(s)]
[Claim 1] Plasma [which is characterized by the surface mean surface roughness which it should be prepared in the environment where a plasma should be used, and it is the member which has corrosion resistance to the aforementioned plasma, and the diameter of mean crystal grain should consist of a 1 to 20 micrometers aluminium-nitride sintered compact, and should contact the aforementioned plasma being 0.5 micrometers or less] anti-corrosion member.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the member used as the member used into the equipment which manufactures semiconductor devices, LCDs, etc., such as a plasma etching system, plasma ashing equipment, and plasma CVD equipment, especially, for example, the member for microwave introduction apertures, a wafer clamper, an electrostatic chuck, a protection plate, etc. about the member which has corrosion resistance to a plasma.
[0002]
[Description of the Prior Art] The equipment which processes using the plasma of a plasma etching system, plasma ashing equipment, plasma CVD equipment, etc. can perform efficient required processing at low temperature, and a control of processing cannot be lacked in a manufacture of high integrated-semiconductor equipment, a LCD, etc. from the point that it is comparatively easy and there are few possibilities of giving a damage to materials, such as a semiconductor substrate,, either.
[0003] Introduce reactant gas in the container which should perform processing decompressed near the vacuum, impress a RF and microwave, a discharge in gases is made to start, and a plasma is made to generate with these equipments. Drawing 1 shows typically an example of this kind of plasma-treatment equipment. In this equipment, it is laid on the sample base 23 and the surroundings of it are surrounded on the protection plate 24. And when a plasma treatment is given to the front face of the material held by the clamper 25, It is CF4, C3 F8, Cl2, and HBr, Ar and O2 from the gas supply spool 13 after performing exhaust air from an exhaust port 14 and setting the inside of the reaction container 11 as a predetermined degree of vacuum to in the plasma production room 20. The reactant gas of a grade is supplied. Cooling water is poured during an operation of equipment at the cooling water circulation room 18, and the circumference of the reaction container 11 is cooled. Microwave is introduced into the dielectric-wire way 12 through a waveguide 15 from a microwave oscillator 16. The electric field are formed in dielectric-wire way 12 lower part by this, and the formed electric field pass the microwave introduction aperture 22, and are introduced in the plasma production room 20. The gas supplied from the gas supply spool 13 is introduced in the plasma production room 20, and is plasma-ized by irradiation of microwave. Among plasmas, a neutral radical mainly passes the mesh-like diaphragm 17, spreads in a reaction chamber 21, and reaches on the surface of a material electrically, and a plasma treatment is given. Moreover, in such equipment, an electrostatic chuck is used as a fixture holding the material which should be carried out a plasma treatment.
[0004] In such plasma-treatment equipment, a microwave introduction aperture, a protection plate, a clamper, an electrostatic chuck, etc. are exposed to a plasma. Therefore, these members need to have corrosion resistance to a plasma.
[0005] For example, it is comparatively chemically stable and there are quartz glass and an alumina ceramics as a material which has thermal resistance. For example, these materials have been used as a microwave introduction aperture etc. in plasma-treatment equipment.
[0006] However, quartz glass is inferior to the corrosion resistance over the reactant gas of a fluoride

system. Moreover, quartz glass tends to penetrate the radiant heat and tends to conduct the radiant heat by the plasma generated in the reaction chamber to other fractions of equipment. Moreover, the quartz also has the problem to which it devitrifies and an intensity falls.
[0007] On the other hand, an alumina ceramics has corrosion resistance to the reactant gas of a fluoride system. However, thermal conductivity of an alumina ceramics is comparatively low, and it is a material with a large coefficient of thermal expansion. For this reason, for the heat by the plasma etc., the temperature of the member which consists of an alumina ceramics tends to rise, and thermal stress tends to generate it there. If comparatively big thermal stress occurs repeatedly, since it will lead to a crash of a crack etc., an alumina-ceramics member cannot desire so long a life.
[0008]
[Problem(s) to be Solved by the Invention] It has gone up to the candidate to the material mentioned above as a material into which an aluminium nitride has corrosion resistance to a plasma. Thermal conductivity of an aluminium nitride is notably higher than an alumina, and it is a material with a low coefficient of thermal expansion. For this reason, by the aluminium nitride, it is thought that occurrence of the thermal stress like an alumina seldom happens.
[0009] The purpose of this invention has the corrosion resistance over a plasma in offering the more excellent member using such an aluminium nitride.
[0010]
[Means for Solving the Problem] this invention person found out that the corrosion resistance over a plasma became high notably, when the mean surface roughness was set to 0.5 micrometers or less, as a result of the corrosion resistance (etch rate) of the member which consists of an aluminium-nitride sintered compact finding out that it is related to the surface roughness of a member and inquiring in the related ****** detail of the surface roughness and corrosion resistance. It is enlarging the diameter of mean crystal grain of the aluminium-nitride sintered compact which constitutes a member in order that this invention person's may furthermore reduce advance of etching by the plasma to some extent, and considering as within the limits of 1-20 micrometers, and found out that the member which is excellent in the corrosion resistance over a plasma, and maintains a high intensity was obtained.
[0011] That is, it is characterized by the surface mean surface roughness which the member which is prepared in the environment where a plasma should be used and has corrosion resistance to a plasma should be offered, and, as for this member, the diameter of mean crystal grain should consist of a 1 to 20 micrometers aluminium-nitride sintered compact, and should contact a plasma by this invention being 0.5 micrometers or less.
[0012]
[Embodiments of the Invention] In this invention, an aluminium-nitride sintered compact can be obtained by usual technique. For example, it responds to aluminium-nitride powder at the need, and is Y2 O3. Alkaline-earth-metal oxides, such as a rare-earth-elements oxide of a grade, and CaO, and YF3 The sintering acid which consists of a rare-earth-elements halogenide of a grade etc. is added, further, media, such as an organic binder and an organic solvent, etc. are added and a slurry is prepared. In this case, AlN powder of a high grade 1000 ppm or less is preferably used for the total amount of a metal impurity as aluminium-nitride powder. You may add and it is not necessary to add a sintering acid. When adding a sintering acid, the addition can be preferably made into 1 - 7 % of the weight 0.1 to 10% of the weight as opposed to the sum weight of aluminium-nitride powder and an assistant. The granulation of the obtained slurry is carried out using a spray dryer etc., and considering as granulation powder is desirable by drying. The obtained granulation powder is fabricated by the golden die forming, the isostatic hydrostatic pressing (CIP molding), etc. A more precise Plastic solid can be obtained by using a hydrostatic-pressure press. After degreasing by heating the obtained Plastic solid, sintering is performed and the aluminium-nitride sintered compact which has a required configuration according to intended use is obtained. Sintering temperature can be made into 1650 degrees C - 1900 degrees C when using a sintering acid. On the other hand, when not using a sintering acid, temperature higher than it, for example, the temperature of 1900 degrees C - 2100 degrees C, is used. The aluminium-nitride sintered compact which has a desired diameter of mean crystal grain can be obtained by adjusting sintering

conditions, such as a modality of sintering acid, temperature, and time, etc.
[0013] The member by this invention is obtained by finishing the front face exposed to a plasma at the time of use to a mean surface roughness 0.5 micrometers or less about the aluminium-nitride sintered compact which does in this way and is obtained. In order to obtain a such very smooth front face, in this invention, a grinding process and/or a polishing manipulation are usually used. A diamond, cBN, SiC, etc. can be used for the abrasive grain used for grinding and polishing. A manipulation grinding stone chooses suitably things, such as a thing of resin bond, and a thing of vitrified bond, and they should just be used for it. About other conditions, such as a working liquid, the usual conditions of being used for the surface treatment of a ceramics can be followed. It is mainly desirable to use for finishing of the abrasive grain of the number of watch beyond **600 to obtain a desired smooth front face by the manipulation by the grinding stone. Moreover, when finishing a front face by polishing finally, 10 micrometers or less can be finished by using an abrasive grain with a particle size of 3 micrometers or less preferably. Generally, it can rough with the grinding stone using the abrasive grain with the low number of watch, and can finish-machine by the grinding stone with the number high subsequently of watch, and the polishing manipulation using the fine abrasive grain can be performed further if needed. In such a case, the abrasive grain beyond **600 can be used for finish-machining at roughing using the abrasive grain of **140-**400. Moreover, 10 micrometers or less of abrasive grains with a particle size of 3 micrometers or less can be preferably used for the polishing for finishing. According to the intended use and the configuration of a member, such manipulation technique can be chosen suitably.
[0014] The corrosion resistance (etch rate) over the plasma of the member which consists of an aluminium-nitride sintered compact improves notably by setting the mean surface roughness to 0.5 micrometers or less as it is shown in the following examples. Etching by the impact of plasma ion is dependent on the collision angle of the plasma ion to an irradiation side. The greatest etching happens at the time of about 45-degree incidence, and becomes more than twice as compared with the time (90 degrees) of a perpendicular. When surface granularity is micro and it sees, it will have an angle to plasma ion. It is a perfect flat surface ideally, and if a plasma is irradiated by 90 degrees, etching will advance uniformly. However, in fact, by flat-surface granularity, the place where etching advances locally can be performed and it becomes the uneven way (way of decreasing with intense irregularity) of decreasing. In this invention, it is decreasing notably by setting to 0.5 micrometers or less the surface mean surface roughness which should contact a plasma in such influence.
[0015] Moreover, even if it is in the same polishing status, pit-like etching advances considering the grain-boundary section, especially the triple point as a center. Then, in this invention, in order to reduce the triple point, the diameter of mean crystal grain in an aluminium-nitride sintered compact is set to 1 micrometers or more, and it is considering as the sintering organization in which corrosion resistance was [that etching seldom advances] excellent. On the other hand, although good corrosion resistance is acquired, the intensity of a member falls and a reliability comes to be missing, when the diameter of mean crystal grain exceeds 20 micrometers as a structural member. Therefore, in this invention, in order to obtain the outstanding corrosion resistance and the outstanding intensity, the diameter of mean crystal grain in an aluminium-nitride sintered compact is made into the domain of 1-20 micrometers. Such a diameter of crystal grain of a domain can be obtained by adjusting sintering conditions, such as the grain size of AlN powder for manufacturing a sintered compact, a modality of sintering acid and an amount, temperature, and time, etc. Generally, the sintering organization which has a desired diameter of mean crystal grain using the sintering acid of a suitable addition by sintering at the temperature of 1750 degrees C - 1850 degrees C can be obtained. It is desirable to, use the sintering temperature of 1900 degrees C - about 2000 degrees C on the other hand, when not using a sintering acid. The temperature and time of sintering can be adjusted so that it may go into within the limits whose mean particle diameter obtained as a result of grain growth is 1-20 micrometers.
[0016]
[Example] Specific surface area was 2.4-3.0m2 / g, the sintering acid was added as the total amount of a metal impurity showed high-grade AlN powder 1000 ppm or less in Table 1 if needed, the binder of a polyvinyl alcohol system was further added in the alcoholic system organic solvent, and the slurry was

prepared. The obtained slurry was corned using the spray dryer. Granulation powder was fabricated with metal mold to 120mmx120mmx10mm, and carried out CIP molding further. It is the obtained Plastic solid N2 It calcinated at 1650-2050 degrees C among the ambient atmosphere, and the aluminium-nitride sintered compact was obtained.

[0017] About the obtained sintered compact, the parallel side manipulation was first performed with the surface grinder. A manipulation grinding stone is a diamond wheel of the resin bond of **170, and, thereby, roughed. Subsequently, it finish-machined using the same grinding stone of **600. The examples 1-5 and the examples 1-3 of a comparison which are shown in Table 1 have all passed through the process shown above. In there, the modality of sintering acid and an addition, and sintering temperature are as being shown in Table 1. Then, in order to grind with a lapping machine using the surface plate made from cast iron by the diamond abrasive grain with a particle size of 10 micrometers and the diamond abrasive grain with a particle size of 3 micrometers and to raise polishing precision further, it finished by the 1-0.5-micrometer abrasive grain using the copper surface plate. In the examples 1-4 and the examples 1 and 2 of a comparison, the polishing by such lapping machine was performed to the last. On the other hand, in the example 5, it ended in the phase which performed the polishing using the 3-micrometer diamond abrasive grain of the polishing by the lapping machine. Moreover, in the example 3 of a comparison, the polishing by the lapping machine was ended in the phase of the polishing using the 10-micrometer diamond abrasive grain. According to the above process, the member of the aluminium-nitride sintered compact with which a mean surface roughness and the diameter of crystal grain of a sintering organization are different, respectively was obtained.

[0018] In each obtained member, the mask of a part of manipulation side was carried out on the fluororesin system tape, and plasma irradiation was presented. Parallel monotonous formula RIE (reactive ion etching) equipment was used for plasma equipment. 13. The RF of 56 MHz, 0.8kW of outputs, and CF4 The plasma was irradiated under etching gas and the condition with a pressure of 5Pa for 1 hour at each member of an aluminium-nitride sintered compact. The mask tape on the front face of a sample was removed after plasma irradiation. The level difference generated between the irradiation section and the non-irradiated section was measured with the sensing-pin formula surface-roughness plan, the irregularity of an etching side was further measured with the atomic force microscope (AFM), and it asked for the etching volume in a 50x50-micrometer field from both sum.

[0019] The mean surface roughness of the member of the aluminium-nitride sintered compact obtained by the manufacturing process mentioned above, respectively, an intensity, and an etching volume after irradiating a plasma about the member are shown in Table 1 with manufacture conditions. A mean surface roughness is 0.5 micrometers or less, its etching volume is small while the examples 1-5 in the domain whose diameter of mean crystal grain is 1-20 micrometers further have a comparatively high intensity, and the corrosion resistance over a plasma has become what was notably excellent as shown in a table.

[0020]

[Table 1]

		焼結助剤		焼結温度	ラップ砥粒	平均結晶	平均表面粗さ	強度	ｴｯﾁﾝｸﾞ体積
		種類	量(wt%)	(°C)	(μm)	粒径(μm)	Ra(μm)	(kg/mm²)	(μm³/min)
実施例	1	Y_2O_3	3	1850	0.5	5.0	0.05	40	16
	2	Y_2O_3	3	1750	1	1.8	0.2	38	25
	3	Y_2O_3	3	1850	1	5.0	0.2	40	22
	4	なし		1900	1	12.0	0.2	30	20
	5	Y_2O_3	3	1850	3	5.0	0.4	40	28
比較例	1	YF_3	3	1650	1	0.8	0.2	35	32
	2	なし		2050	1	22.0	0.2	15	18
	3	Y_2O_3	3	1850	10	5.0	0.7	40	42

[0021]
[Effect of the Invention] According to this invention, the member which is excellent in the corrosion resistance over a plasma, and has a comparatively high intensity can be offered. Since the member by this invention has the outstanding corrosion resistance which big thermal stress seldom generates and was mentioned above since it was what consists of an aluminium-nitride sintered compact, it can have a life longer than the former. The plasma anti-corrosion member by this invention is useful as the member used for the equipment which manufactures semiconductor devices, such as an etching system, ashing equipment, and a CVD system, a LCD, etc., for example, a microwave introduction aperture, a wafer clamper, an electrostatic chuck, a protection plate, etc.

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DESCRIPTION OF DRAWINGS

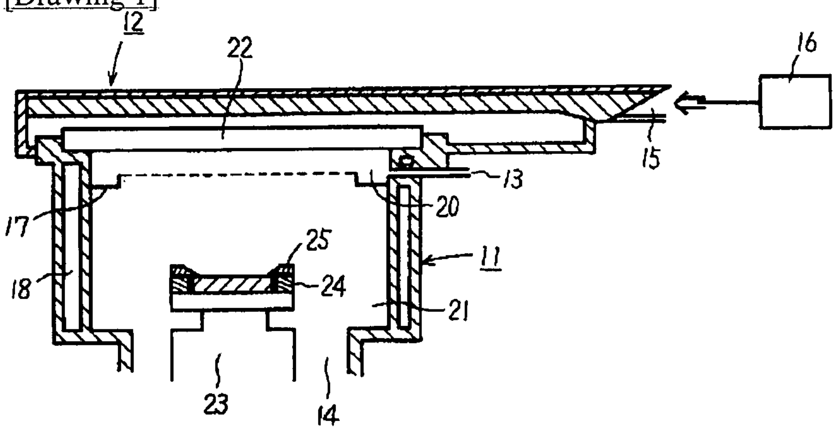
[Brief Description of the Drawings]
[Drawing 1] It is the cross section showing an example of plasma-treatment equipment typically.
[Description of Notations]
22 Microwave Introduction Aperture
24 Protection Plate
25 Clamper

[Translation done.]

* NOTICES *

DRAWINGS

[Drawing 1]



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